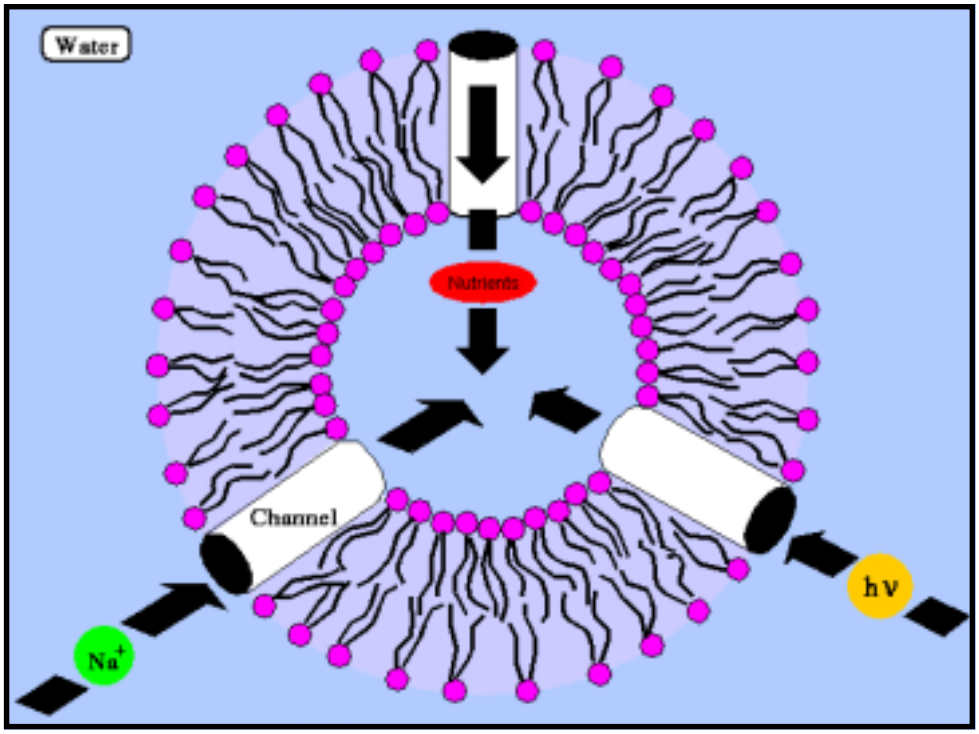

Basic Cell Structure. Credit: Andrew Pohorille

Exobiology Branch (SSX) Overview

The Branch's research focuses on the advancement of the scientific understanding of the origin and distribution of life by conducting research on the cosmic history of biogenic compounds, prebiotic evolution, and the early evolution of life. This is accomplished via laboratory experiments, theoretical studies/computational modeling, and field investigations. Branch personnel are also involved in the development of flight instruments, experiments, and small mission definition with particular emphasis being placed on studies of Mars and the development of instrumentation for martian flight missions. Several Branch scientists are part of a task module that is a component of the Ames membership in the Astrobiology Institute. Branch scientists provide expertise in exobiology, astrobiology, planetary protection, and other areas of planetary science to NASA Headquarters and external review and advisory panels, and some serve as editors and associate editors of scientific journals.

Exobiology studies includes the history, distribution, and chemistry of biogenic elements in the solar system; prebiotic chemical evolution and the origin of life; and the history of Earth's early biosphere as recorded in microorganisms and ancient rocks. The research is conducted both on Earth and in space. The Branch also serves as the center of expertise within the agency for issues of planetary protection. As the agency lead center in exobiology, Branch exobiologists exercise a leadership role in NASA's Exobiology Program through program planning, performance reviews, advisory services to related NASA programs, and external relations.

David F. Blake

Chief, Exobiology Branch (SSX)

A GREENHOUSE COLLABORATORY

Brad Bebout and Richard Keller

The Ames Microbial Ecology / Biogeochemistry Research Lab, in combination with the ScienceDesk team, has made significant progress in realizing a greenhouse "collaboratory" which will be shared by members of the NASA Astrobiology Institute's Early Microbial Ecosystems Research Group (EMERG). The greenhouse facility is being used to maintain field-collected microbial mats, as well as perform manipulations of these mats. Microbial mats, extant representatives of Earth's earliest ecosystems, are highly dynamic communities of microorganisms exhibiting extremely high rates of metabolic processes. Maintaining the structure and function of these communities outside of the natural environment is therefore a challenge. Using the greenhouse constructed on the roof of building N239, mats that resemble naturally occurring communities have been maintained over a year after field collection. This year, it was determined that the greenhouse-maintained mats sustain natural rates of biogeochemical processes. This facility, therefore, is useful to support continued measurements of the rates and conditions under which various trace gases are emitted and / or consumed by microbial mats and stromatolites. The greenhouse mats will be used to investigate the effects of early Earth environmental conditions on the rates of trace gas production and consumption in the microbial mats, a period of Earth's history no longer available to us for direct measurement. These measurements are also relevant to the search for life on extrasolar planets, where the most promising search strategy involves the detection of possibly biogenic gases using infrared spectrometry. Space-based interferometers, such as the Terrestrial Planet Finder, should be able to resolve the spectra of several biologically important trace gases in the atmospheres of extrasolar planets, possibly within 10-15 years.

The greenhouse represents a unique facility and a unique resource to be shared among EMERG team members. The team's scientific objectives require multiple collaborators to conduct and analyze measurements of mat parameters on a frequent basis over many weeks. However, pragmatics and funding constraints inhibit the productivity of the distributed team and prevent full utilization of the greenhouse. The construction of a collaboratory – in which human scientists and intelligent agents work together to perform experiments – will alleviate demanding proximity and time requirements that effect productivity. Rather than placing the burden solely on local team members, a collaboratory will enable an entire distributed investigator team to share responsibility for experimentation and data collection.

With this motivation in mind, we have begun construction of a collaboratory designed to enable the geographically distributed group of EMERG scientists to plan greenhouse experiments, operate scientific equipment, take experimental measurements, share results, and collaborate in real time with remote colleagues. Intelligent software agents will assist in the experimentation process, controlling the hardware, recording results, and interacting with the scientists via email. As part of the initial hardware development for the collaboratory, an X,Y,Z positioning table which is capable of

automatically positioning sophisticated instruments at any location in the mats has been constructed. The instrument package currently includes microelectrodes, a light sensor, chlorophyll fluorometer, a surface detection device, and a fiber optic spectrometer. The positioning system, and the instrumentation package is viewable over the internet (http://greenhouse.arc.nasa.gov) via a webcam hooked up to a computer located in the greenhouse. Next implementation steps involve controlling the positioning table and equipment remotely over the internet. ❑

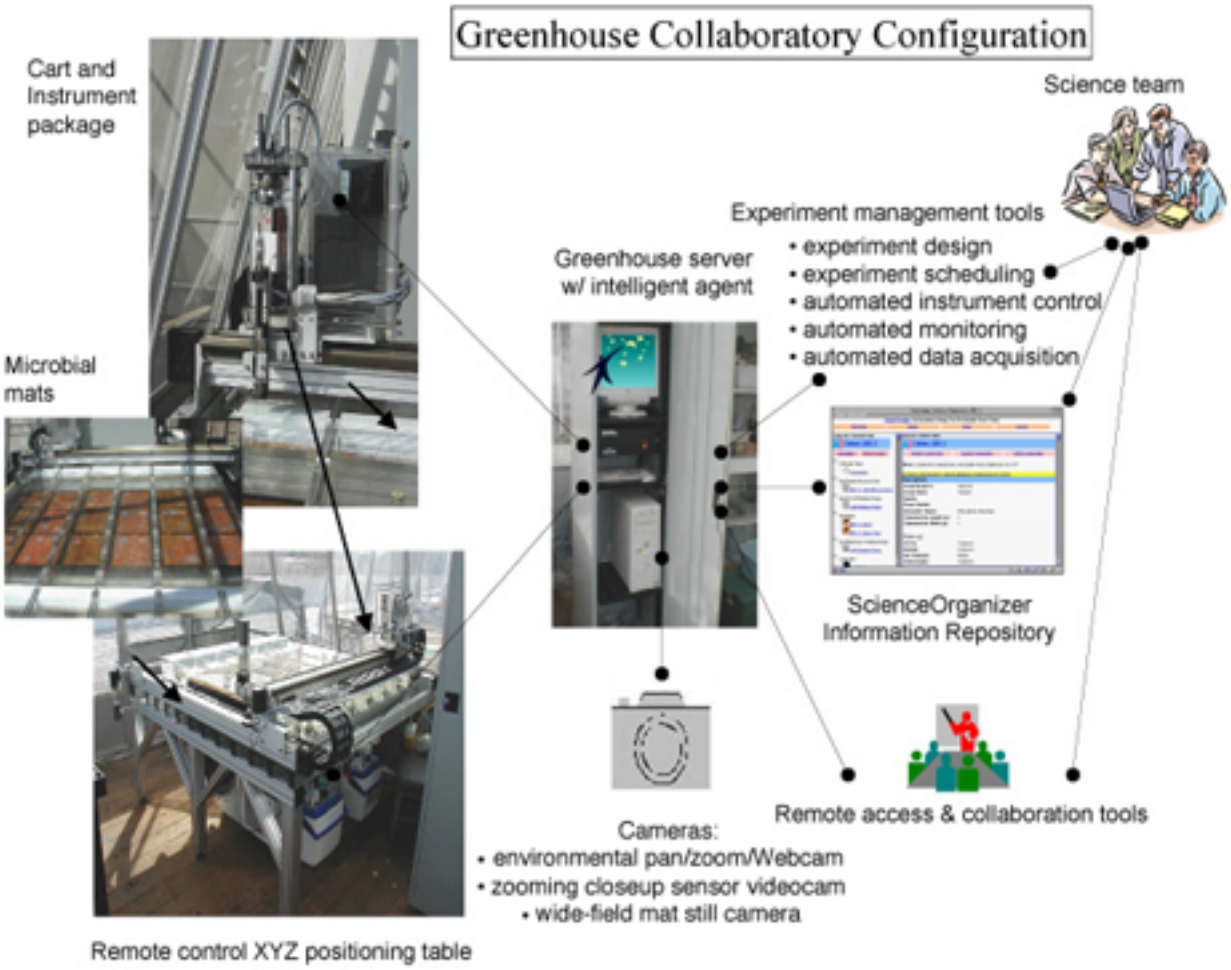

Figure 16: Diagrammatic representation of the greenhouse collaboratory with photographs of the hardware already in place.

CHEMIN: A MINERALOGICAL INSTRUMENT FOR MARS EXPLORATION

David F. Blake

The identification of the types of rocks on Mars that may harbor evidence of present or past life (i.e., biomarkers) will require *in situ* mineralogical analysis. In order to establish the conditions under which a rock formed, the identity of each mineral present and its amount must be determined. In terrestrial laboratories, X-ray Diffraction and X-ray Fluorescence (XRD / XRF) are the techniques of choice for such characterizations.

Recent progress in X-ray technology allows the consideration of simultaneous X-ray diffraction (XRD: mineralogic analysis) and high-precision X-ray fluorescence (XRF: chemical analysis) in systems scaled down in size and power to the point where they can be mounted on landers or small robotic rovers. The CHEMIN XRD / XRF instrument, which simultaneously collects XRD and XRF data, has been proposed in the past for a variety of solar system missions and is presently proposed for three separate Mars scout missions, including a precision lander, a penetrator and a lander equipped with a drill.

NASA was awarded a patent in 1996 (US Patent No. 5,491,738) for the CHEMIN concept. The instrument received a commercial "R&D 100 award" as one of the top 100 innovative technologies of 1998. A SBIR (Small Business, Innovative Research) phase II proposal has been awarded to Moxtek, Inc. to build and commercialize a laboratory version of CHEMIN.

CHEMIN is a CCD-based simultaneous X-ray diffraction / X-ray fluorescence instrument. The device is designed to characterize the elemental composition and mineralogy of small fine-grained or powder samples. The name CHEMIN refers to the instrument's combined CHEmical and MINeralogic capability.

Both diffraction and fluorescence data are obtained simultaneously by operating the CCD in single-photon counting mode. Energy discrimination is used to distinguish between diffracted primary beam photons and fluorescence photons. Diffraction data are obtained in transmission mode, and resolution is presently sufficient on the prototype instrument to allow application of the Rietveld refinement method to the diffraction data. X-ray fluorescence data will be obtained for all elements, $4<Z<92$.

A diagram of the proposed CHEMIN flight instrument is shown in Figure 17. In operation, the carousel of the instrument (which is the only moving part) is rotated to place one of 40 collection grids in a position to receive a soil sample or a sample of drill cuttings from a rock. The carousel is then rotated to place the grid in the analysis position between the X-ray source and CCD. A combination of carousel rotation and 1-2 mm motion along the x-axis allows the entire substrate to be sampled sequentially by the X-ray beam. An intelligent systems program determines the location of sample material suitable for analysis and supervises data collection.

A prototype of the CHEMIN instrument has been operable since July 1996. After optimization of the X-ray source collimation, diffraction data were obtained in the Fall of 1996 of sufficient quality to be used with advanced diffraction data analysis methods such as Rietveld refinement. Various sample handling systems are presently being pursued, and designs have been proposed for terrestrial use in commercial laboratories, in the International Space Station, and in the proposed Mars Sample Return Handling Facility. ❑

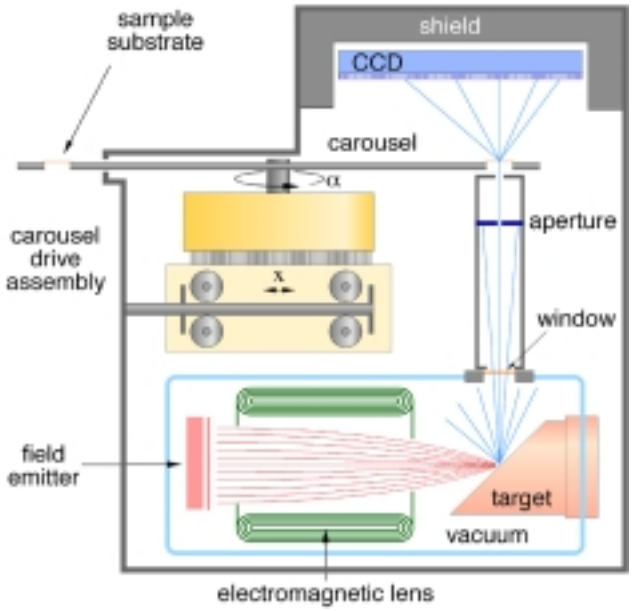

Figure 17: Cross-sectional diagram of the proposed CHEMIN flight instrument.

SUGAR-RELATED COMPOUNDS IN METEORITES

George Cooper, Novelle Kimmich, Josh Sarinana, Katrina Brabham,
Laurence Garrel, and Warren Belisle

A goal of NASA is to understand the origin and evolution of life. Carbonaceous meteorites provide the only record yet available for the laboratory study of organic compounds that were synthesized very early in the Solar System and delivered to the planets. Until now sugars and related compounds (polyols), one the most critical classes of compounds necessary for all current lifeforms, had not been definitively identified in extraterrestrial samples. Ribose and deoxyribose, five-carbon sugars, are central to the role of contemporary nucleic acids, DNA and RNA. Glycerol, a three-carbon sugar alcohol, is a constituent of all known biological membranes. Part of the scientific research performed at Ames is directed towards determining if such compounds are part of the organic content of meteorites. This report described the results of the search for such compounds.

Results are reported from analysis of water extracts of the Murchison and Murray carbonaceous meteorites. The means of identification of compounds was gas chromatography-mass spectrometry (GC-MS). Compounds were prepared for GC-MS as their trimethylsilyl and / or tertiary butyl-dimethylsilyl derivatives. Our analyses of Murchison and Murray extracts show that a variety of polyols are present in carbonaceous meteorites (Figure 18). The identified compounds include a sugar, dihydroxy acetone; sugar-alcohols; sugar mono-acids; sugar di-acids; and "deoxy" sugar acids (or "saccharinic" acids). In general the compounds follow the abiotic synthesis pattern of other meteorite classes of organic compounds: decreasing abundance with increasing carbon number within a class of compounds and many, if not all, possible isomers are present at a given carbon number.

A plausible synthetic origin for at least of some of the polyols in Murchison and Murray is the photolysis of interstellar gases on interstellar grains. Another possible origin is the condensation of alkaline aqueous solutions of formaldehyde – which is known to produce polyols. Formaldehyde is a relatively abundant and ubiquitous molecule in interstellar space and comets. Extracts of Murchison and Murray show that the aqueous solution on the parent body(ies) was slightly alkaline. Once produced, further chemistry under alkaline and / or oxidizing can oxidized sugars to a variety of acids of the type in Figure 18.

The fact that a suite of related sugar derivatives and dihydroxyacetone are present in meteorites makes it likely that more sugars were, at one time, also present. Other bodies (comets or asteroids), perhaps in different stages of aqueous alteration or oxidation, may have delivered intact sugars to planets in the early Solar System. However dihydroxyacetone alone is capable of producing larger sugars in aqueous solution. The finding of these compounds in some of the oldest objects in the Solar System suggests that polyhdroxylated compounds were, at the very least, available for incorporation into the first living organisms. ❑

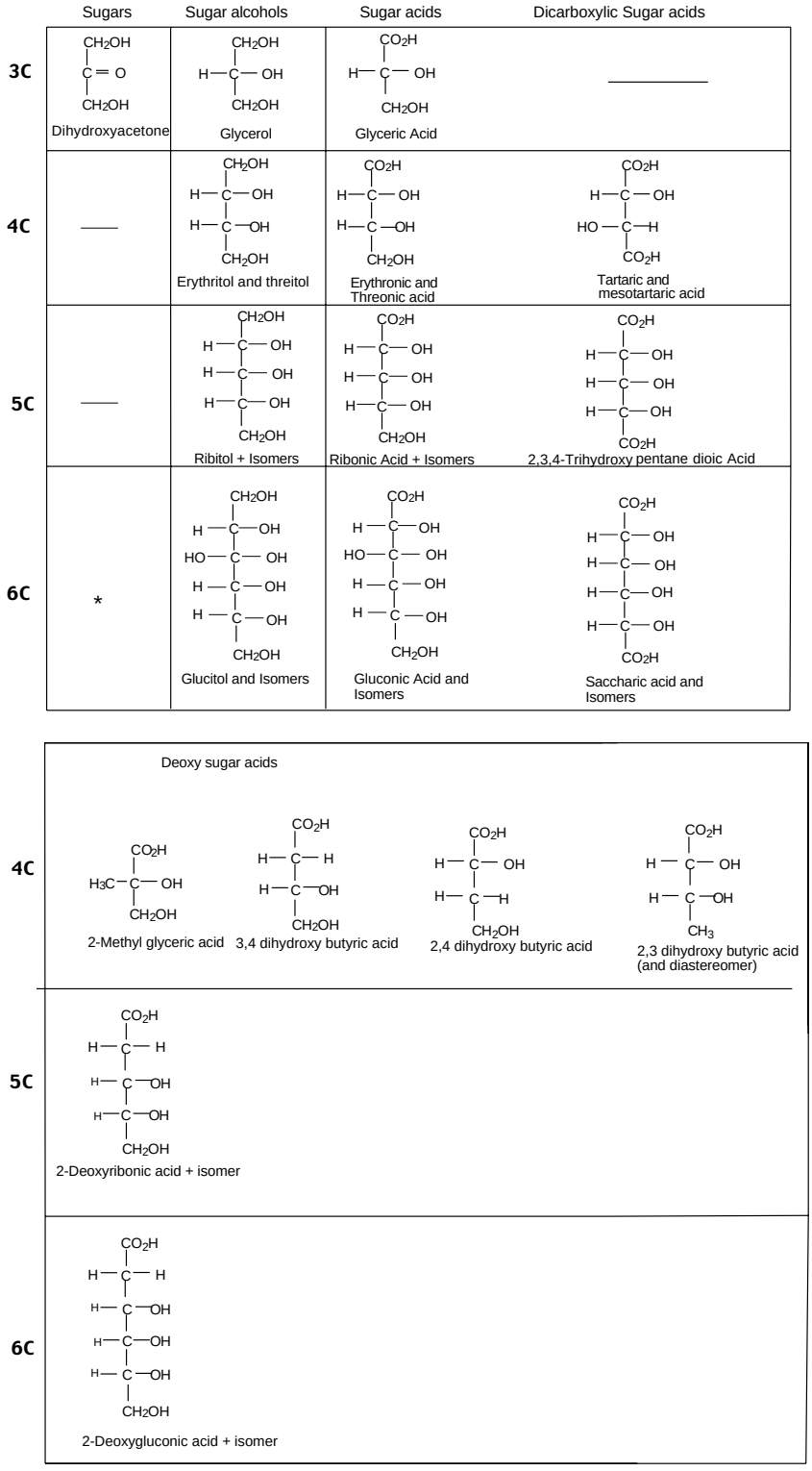

Figure 18: Polyols identified in the Murchison and Murray carbonaceous meteorites. Compounds were identified by gas chromatography-mass spectrometry as their trimethylsilyl and/or tertiary butyl-dimethylsilyl derivatives. *6-C Sugars monomers were not seen but may be present in bound forms.

EFFECTS OF DISTRUBANCE ON MICROBIAL COMMUNITIES

Ken Cullings

This research addresses Astrobiology Objective 14 which deals with ecosystem responses to disturbance. Functional biodiversity results from both absolute species numbers in any ecosystem and interactions among members of the community, and plays a pivotal role in the resilience of ecosystems to disturbance and environmental change. Ecosystem reliability can increase when the number of species per functional group increases, thus illustrating the value of functional redundancy or similarity in an ecosystem. On the other hand, gains or losses of species that perform different functions can cause ecosystem processes to be significantly altered. Thus, a controversial aspect of functional diversity is whether species exhibiting similar function are actually redundant, and thus expendable.

This research targets microbes, and a common view is that the potential for redundancy or similarity among microbial species is high. Specifically, we focus on one pivotal mutualistic interaction, the ectomycorrhizal (EM) symbiosis, a plant/fungal interaction that controls both carbon and nitrogen cycles in forest ecosystems. This research has two steps. First, to assess changes in the EM community in response to disturbance. Second to determine if there are functional changes in the ecosystem that results from any changes.

1) Artificial Defoliation (manuscript in press at Oecologia). No previous study has been conducted of effects of altered carbon available to roots in systems comprised of more than a single tree species. Results indicated no significant effect on either EM colonization or on species richness. However, the relative abundance of EM of the two tree species shifted from a ratio of approximately 6:1 without treatment (lodgepole EM:spruce EM), to a near 1:1 ratio post-treatment. In addition, EM species composition changed significantly post-defoliation. Species of EM fungi associating with both lodgepole pine and Engelmann spruce were affected, indicating that alteration of photosynthetic capacity of one species can affect mycorrhizal associations of neighboring non-defoliated trees. Finally, while some fungal species may exhibit consistent specificity patterns (for example Suillus tomentosus to P. contorta) other fungal species shifted host preference in response to the change in source of fixed carbon induced by defoliation.

2) Effects of litter addition on a stand of pure lodgepole pine, P. contorta, (data complete, manuscript to be submitted to Oecologia). Molecular analyses indicate that 1) litter addition significantly increases EM infection levels in the top soil layer, directly adjacent to the added litter. No change is seen with perlite addition. Thus, this response is due solely to nutrient changes imposed by litter; 2) the EM community is altered significantly by litter addition. Species dominant in controls may be lost in response following treatment, and some species increase only in response to litter but not to perlite, further illustrating the role of changes in nutrient status.

3) Effects of litter removal on a mixed lodgepoile pine / Engelmann spruce (P. engelmannii) stand (data are complete, manuscript is in preparation): Results of molecular analyses indicate that, 1) litter removal significantly decreased EM fungal species richness, from 3.0 to 1.5 species / core; 2) as expected from previous studies that indicate that increased nitrogen in litter can inhibit EM infection, litter removal induced a significant increase in EM infection, from a mean of 228 EM / core in controls to 326 in treatments; 3) furthermore, molecular analyses indicate that while many basidiomycete fungal species are common to both treatments and controls, the ratio of basidiomycetes to ascomycetes changed significantly in response to litter removal, from 12:1 ratio of basidiomycete to ascomycete EM, to a 3:1 ratio.

Together, these results indicate that these disturbances can causes changes in the EM fungal community. Because different species may perform different functions, these results indicate that it is now necessary to assess changes to pivotal ecosystem functions. Thus, our next step will be to perform assessments of changes in enzyme systems that are responsible for controlling both nitrogen and carbon cycles in forest ecosystems. ❑

CARBON NANOTUBE DEPOSITION AND GROWTH TECHNIQUE

Lance Delzeit

Carbon nanotubes (NTs) possess electrical, mechanical and physical properties that make them ideal for applications in nanotechnology. A major constraint to the realization of many of these applications is the ability to produce nanotubes in an industrially viable method with the characteristics desired for the given application. A few of these characteristics include quantity, chirality, size, density, distribution and purity of the nanotubes produced. The research described here focuses on the production of NTs with the desired density, distribution, and purity for the application to industrially viable products.

A catalyst deposition and growth technique has been developed that allows for the controlled growth of either single- or multi-walled carbon nanotubes. This technique uses ion-beam sputtering to deposit the catalyst. By changing the catalyst formula and the growth conditions, either single- or multi-walled carbon nanotubes can be grown. Furthermore, by adjusting the conditions used to produce single-walled nanotubes, the density of the nanotubes grown can be controlled from a sparse distribution of individual single-walled nanotubes to dense mats of single-walled nanotube “ropes”. “Ropes” are an association of individual nanotubes that forms a larger structure just as individual fibers make up a normal rope. The conditions for the growth of multi-walled nanotubes have been optimized for the growth of “towers”. A “tower” is a structure in which the nanotubes grow in the vertical direction because of the high density of the nanotubes in that region. These different structures each have applications to a variety of devices.

A further advantage of this technique is the ability to pattern the catalyst onto the surface. If the application requires the nanotubes to be grown in a confined area, then the ability to restrict the deposition of the catalyst to those areas is critical. This process, with the use of standard shadow masking and lithography techniques, has the ability to create such patterned catalyst deposits for the development of applications.

Finally, for most applications, the nanotubes need to be produced free of impurities and contamination. The two major sources of contamination in the growth of carbon nanotubes are: 1) the build-up of amorphous carbon from the extraneous decomposition of carbon feed gas and 2) contamination by extraneous metal catalyst. The elimination of the extraneous metal catalyst is currently being accomplished by optimizing the catalyst formula, thus reducing the quantity of "inactive" catalyst. The removal of the amorphous carbon is being realized by the use of etching gases that preferentially removes the amorphous carbon while not damaging the carbon nanotubes. ❑

STRUCTURE AND FUNCTIONS OF PROTOCELLS

Andrew Pohorille and Michael A. Wilson

This research is devoted to the origin of cellular functions, with a long-term objective to explain how protocells performed functions essential for their survival and evolution utilizing only molecules that may have been available in the protobiological milieu. Simple models of several protocellular functions have been developed, and computer simulations have been carried out using molecular dynamics (MD) computer simulations. In MD simulations, Newton's equations of motion are solved for all of the atoms in the system under study, providing a complete time-history of the system. Properties of interest are computed from the trajectory using classical statistical mechanics.

Protocells and their functions: Probably the first cell-like structures were vesicles - closed, spheroidal assemblies of organic material enclosing an aqueous medium. The walls of vesicles are built of amphiphilic molecules which have water-soluble (hydrophilic) and water-insoluble (hydrophobic) groups at opposite ends. These molecules are arranged in bilayers such that the hydrophilic head groups point toward water and the hydrophobic tails form the interior of the bilayer. In this respect, vesicle walls resemble modern cell membranes. Under proper conditions, vesicles form spontaneously from an aqueous solution of amphiphiles. Vesicles became the precursors to true cells - protocells - by acquiring the capabilities needed to survive and reproduce. Protocells had to transport ions and organic matter from the environment across their walls, capture and utilize energy, and synthesize the molecules necessary for self-maintenance and growth. The identity of molecules that performed these functions is open to debate. As most metabolic functions In modern organisms are carried out by proteins, the most parsimonious assumption is that their protobiological precursors were peptides. Their protocellular potential is illuminated by the fact that a wide range of simple, naturally occurring or synthetic peptides can spontaneously insert into membranes and assemble into channels capable of transporting material across cell walls.

Results: The stability of monomers and dimers of a peptide consisting of leucine (L) and serine (S) in a heptad repeat arrangement of $(LSLLLSL)_3$ has been investigated in a membrane-like system consisting of an octane layer between two water layers. Both the transmembrane and parallel, in-plane orientations of the monomer correspond to stable states, with the parallel orientation being more stable. However conversion between the two requires crossing a large free energy barrier and requires substantial structural rearrangement of the water molecules on both sides of the membrane.

While a transmembrane dimer was found to be stable, a dimer oriented parallel to the interface was found to be unstable. This implies that the predominant state of an equilibrium distribution of peptides is a monomer parallel to the interface. Under the application of an external electric field, the monomers rotate into the transmembrane orientation, where they can aggregation into dimers and tetramers. Experiments in other laboratories have demonstrated that tetramers can function as channels for transporting protons across the membrane.

One goal of this research project is to construct multimeric, transmembrane structures that can function as primitive catalysts. In the present case, the peptide does not possess interactions that are specific enough to maintain a rigid structure that could contain a catalytic site. This is due to the fact that the transmembrane dimer structure, as shown in Figure 19, is much less rigid than a coiled-coil structure. It has been observed more generally that transmembrane proteins are not simply "inside-out" analogues of water soluble proteins. Consequently, specific residues must be modified to achieve the packing that is typical of water-soluble coiled-coils. ❑

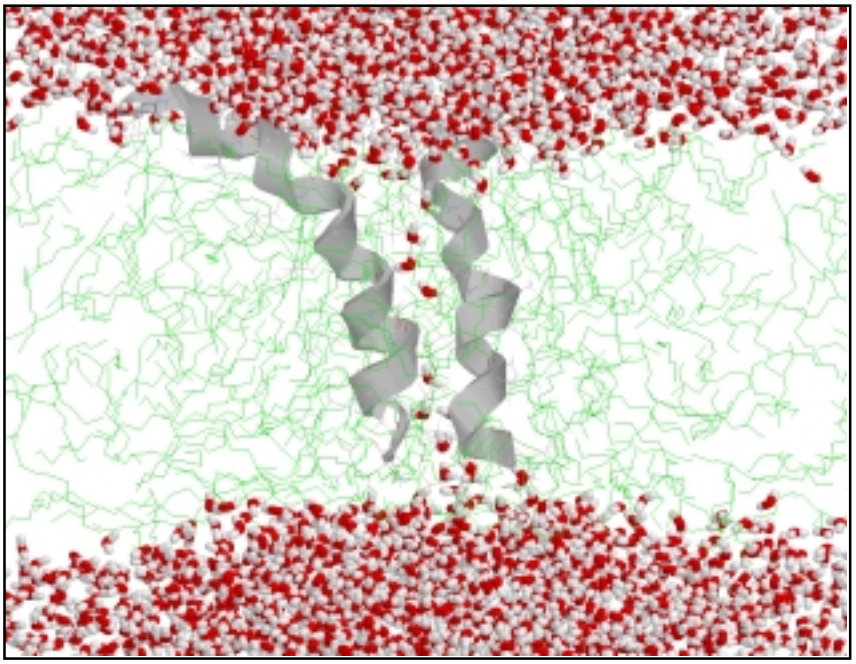

Figure 19: Transmembrane dimer of $(LSLLLSL)_3$. The peptide molecules are show as gray helices, the octane is green and the water is red and white. The disorder is evidenced by the separation of the helices and the significant water penetration into the membrane interior.

MICROBIAL ECOSYSTEM STRUCTURE

Lee Prufert-Bebout

The Ames Geobiology and Ecosystem Structure Laboratory is a new facility which was initially established in late Summer 2000. The research goals of this laboratory are to contribute to our understanding of the spatial distribution of microbes in biofilms, microbial mats and stromatolites and to understand how these distribution patterns are recorded in the rock record. Spatial distribution of microbes is of critical importance in facilitating the transfer of gaseous and dissolved compounds both between microorganisms and between microorganisms and their environment. As microorganisms are motile and can in effect position themselves where conditions are most advantageous, their distribution patterns offer key clues as to how these ecosystems function. The old adage is that "everything is everywhere, but the milieu selects." Understanding how microbes react to the milieu via their physical distribution is therefore absolutely key to interpreting modern, ancient and extraterrestrial microbial ecosystems.

However, most microbial ecology research approaches are not designed to address this issue. Microbes cultivated as single organism populations in a test tube will not behave in the same manner as those in mixed microbial population assemblages in natural environments. There microbial populations experience fluctuations in irradiance, water flow and chemical environment seldom, if ever, seen in a laboratory environment. Monitoring of natural ecosystems offers clues to as to how ecosystems function, but the large number of variables operating at any given time, prohibit rigorous scientific manipulation and testing. Our goal is to bridge this gap by conducting controlled, mixed microbial ecosystem experimentation.

The first series of experiments in the Geobiology and Ecosystem Structure laboratory has documented that given an initial, homogeneous distribution, within carbonate sediments, four different cyanobacterial isolates will repeatedly segregate themselves with distinctly different distribution patterns. However, the actual distribution patterns observed are a function of speed of water flow, permeability of sediments, availability of nutrients and irradiance conditions. Hence it is possible to control the degree and pattern of lamination occurring in these sediments. The cyanobacteria used in these experiments are cultures isolated from modern stromatolites. This approach provides a powerful tool for interpreting the distribution patterns of these cyanobacteria in their natural environment, which to a great extent causes the formation of the laminated fabric of actively lithifying stromatolites. Some of these microbes act as binding agents holding sediments together, while others are active agents in the precipiation of new mineral components which convert the biological ecosystem into a lithified structure which can be preserved in the rock record. Understanding the controls of formation of these laminated fabrics in modern stromatolites is a first step in improving the interpretation of lamination biosignatures in ancient stromatolites from Earth and potentially laminated rocks from extraterrestrial sources. ❑

RINGDOWN CAVITY FOR ISOTOPIC RATIO MEASUREMENTS OF CARBON AND OXYGEN

Todd Sauke and Joe Becker

Molecular and isotopic spectroscopy in the mid-infrared (3 - 7 micrometer wavelength) has been extremely useful for many quantitative gas detection applications in fields as diverse as astrobiology, geology, atmospheric science, pollution control, environmental monitoring, and industrial process control. Variations in isotopic ratios of $^{12}C/^{13}C$ and $^{16}O/^{18}O$ in Martian soil samples could be important clues to the planet's geologic and biologic history. Such variations would be expected to be generated in a sample by any process of elemental transfer whose rate limiting step is diffusion controlled. This could include past or present volcanism, freeze thaw cycles, incorporation of carbon dioxide into the soil from the Martian atmosphere, enzymatic reactions, or respiration. Isotopic variability could also be caused in a sample by its having been mixed with other reservoirs of carbon or oxygen.

The typically strong absorption lines in the mid-infrared spectral region allow for sensitive detection without the need for complex, alignment sensitive, multipass sample absorption cells. The diode laser light sources used for spectroscopy in this spectral region typically require cryogenic cooling making them difficult, cumbersome and expensive, limiting their usefulness. On the other hand, in the near-infrared at 1.3 and 1.55 micrometer wavelengths, where inexpensive room temperature laser sources are readily available, the molecular absorption lines are orders of magnitude weaker than those in the mid infrared and can only be used with long path multi-pass absorption cells. Typical long path multi-pass cells, such as White cells, Harriot cells, etc. are large, cumbersome, and alignment sensitive. The relatively new technique of cavity ringdown spectroscopy affords another solution to the problem of achieving very long effective absorption pathlengths.

Laser spectroscopy offers important advantages over conventional mass spectrometry for measurements on a planet's surface. Importantly, because of the high spectral resolution of the laser spectrometer, the detailed and complex sample preparation and purification required for reliable mass spectrometry is unnecessary, because contaminant gasses do not interfere with the measurement. The goal is to develop a prototype instrument for laser spectroscopic isotope analysis of planetary soils and ices on possible missions to Mars and / or Europa.

This project makes use of a ringdown cavity to provide the ultra long effective pathlength needed for spectroscopy with weak infrared absorption lines, but will achieve high light throughput and high spectral resolution by locking the ringdown cavity to the narrow spectral linewidth of a diode laser source.

We have designed and constructed a near-infrared spectrometer consisting of a 1.6 micrometer near-infrared room temperature diode laser, an optical isolator, a spatial filter, and a tuned ringdown cavity which ultimately will be frequency locked to the continuous wave laser source, affording both high spectral resolution of isotopic absorption lines and high optical throughput for high sensitivity measurements. ❑

PREBIOTIC PEPTIDE SYNTHESIS

Arthur L. Weber

About four billion years ago on the primitive Earth chemical processes yielded molecules that had the ability to make copies of themselves (self-replicate). Over evolutionary time these replicating molecules developed into the DNA-protein replicating system of modern life. Although the DNA molecule has a structure that makes it an excellent self-replicating molecule, DNA's structure is too complex to have been synthesized by chemical processes on the early prebiotic Earth. This difficulty with the prebiotic synthesis DNA has led to a search for simpler replicating molecules. One of the best candidates for a primitive replicating molecule are small proteins – called peptides. Peptides are considered good candidates because they are constructed from very simple building blocks – activated amino acid molecules – that could have been made by chemical processes on the primitive Earth. To understand the prebiotic processes on the early Earth that could have generated replicating molecules, such as peptides, we have (1) experimentally studied plausible prebiotic chemical processes that have the potential to yield peptides and other replicating molecules from very simple chemical ingredients such as formaldehyde and derived sugars, and (2) analyzed the thermodynamics of carbon chemistry to establish which types of organic reactions are energetically favorable or unfavorable under mild aqueous conditions.

Since earlier studies by us and other investigators have indicated the involvement of amino acid and peptide thioesters in prebiotic peptide synthesis, we developed a new, very simple method for preparing peptide thioesters that involves the reaction of a thiol molecule with amino acids activated by reaction with the commercially available reagent (carbonyldiimidazole). This synthetic method was used to prepare peptide thioesters from three and eight amino acids in length for several different amino acids. Chromatographic techniques were developed that allowed measurement and purification of the peptide thioesters. This new synthetic method provides an uncomplicated way to generate peptide thioesters for studies of peptide replication.

To identify and understand the chemistry that could have been involved in the origin of the earliest replicating molecule under mild aqueous conditions, we calculated the energy values for the chemical changes that occur in carbon groups undergoing redox reactions and carbon-carbon bond cleavage reactions. We discovered that the energy of redox reactions involving hydrogen transfer between carbon groups is mainly determined by the type of functional group that donates the hydrogen equivalents, with the energy becoming less favorable in the order: aldehydes, formic acid, alcohols, and hydrocarbons. We also found (1) that the cleavage energy of carbon-carbon bonds is primarily determined by the type of functional group that donates the shared electron-pair during cleavage, with the cleavage energy becoming less favorable in the order: carbonyls (ketones, aldehydes), carboxylic acids, alcohols, hydrocarbons, and (2) that the cleavage energy is more favorable when the shared electron-pair is transferred from a more oxidized to a more reduced carbon group, except for bonds between a carbonyl group and a carboxylic acid group where the reverse transfer is more favorable. From the energy of each cleavage reaction we also estimated the energy of its corresponding synthesis (or reverse) reaction that has an energy equal to the negative of the cleavage energy. From these studies we concluded that the chemistry of the origin of life and the structure of metabolism are constrained and limited by the strong dependence of the energy of carbon group transformations on the type of functional group(s) participating in the transformations. ❑